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Predicting Mechanical Strength of In-Use Firefighter Protective Clothing Using Near-Infrared Spectroscopy

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Abstract

The exact lifespan of in-use firefighter protective clothing is difficult to predict due to the large variations in use between individual garments. Furthermore, testing methods used to evaluate new protective clothing are destructive in nature and could not be applied to in-use garments. Various non-destructive techniques have been proposed for the evaluation of in-use clothing, each possessing its own advantages and disadvantages. The ability of near-infrared spectroscopy to predict the tensile strength of thermally aged fabrics used in protective clothing for wildland firefighters and other workers is investigated here. Fabrics were exposed to heat fluxes from 10 to 40 kW/m^2 for various durations using the cone calorimeter, after which the tensile strength of the fabrics was measured. Temperatures measured during the exposures and results of thermal gravimetric analysis tests were used to interpret changes in tensile strength. Multivariate linear regression was used to develop correlations between the tensile strength and the reflectance values measured between 1500 and 2500 nm for new and thermally aged fabrics. It was found that models based on reflectance measurements made at as few as three wavelengths could be used to estimate the tensile strength of the thermally aged specimens.

Keywords: firefighter, protective clothing, durability, non-destructive testing, thermal ageing, near infrared spectroscopy

Introduction

The lifespan of in-use firefighter coats and pants, referred to as firefighter protective clothing in this paper, is affected by many factors including the weight and structure of the fabric, frequency of use, the length and intensity of thermal exposures and contact with hazardous substances [1]. Minimum requirements for the performance of new protective clothing have been clearly established by various national and international standards to ensure the reasonable safety of firefighters (e.g., CAN/CGSB 155.1 [2] and NFPA 1971 [3]), however, there are no clear guidelines on the requirements for the continuing performance of the garments. The National Fire Protection Association (NFPA) and some protective clothing manufacturers state limits after which a garment should be permanently retired (e.g., [4],[5]), but the actual lifespans have been shown to vary greatly depending on the history of use of individual garments. This means some garments may not provide sufficient protection up until the nominal retirement age. Vogelpohl observed this in her examination of used turnout coats; some coats which had been used in firefighting service for less than five years had degraded to a point where they were no longer able to meet the NFPA 1971 requirements for new protective garments [6]. The majority of current methods used to evaluate protective garments are destructive in nature, rendering them unsuitable for testing in-use clothing. Therefore, a need exists to develop non-destructive testing methods to evaluate in-use protective clothing.

Structural firefighter protective clothing is composed of three layers: an outer shell, a moisture barrier and a thermal liner. Testing can be performed on all three layers separately, or together as an ensemble, to evaluate how the material(s) respond to wear, thermal ageing, ultra-violet (UV) light and many other factors. In particular, the outer shell has undergone much testing since it is designed to separate from the other layers. A literature review summarizing the results of tests performed on protective clothing shows that an outer shell's mechanical properties are significantly impacted by ageing, while some other properties such as thermal protective performance (TPP) may experience only slight negative changes and sometimes even positive changes [7]. In other words, changes in the mechanical properties of a garment's outer shell may act as a precursor to other changes occurring in the ensemble. For these reasons, methods of non-destructively testing the mechanical properties of a garment's outer shell are of interest for determining the condition of the entire garment. In wildland firefighting, garments such as protective coveralls are used instead of the three-layered structural firefighting ensemble; these coveralls are made of fabrics which have lower surface weights than outer shell materials, but are chemically similar. Therefore, wildland firefighting garments could be non-destructively tested via the same procedure as outer shells for structural firefighting.

Several non-destructive techniques have been proposed for the evaluation of mechanical properties of in-use protective clothing, including Raman spectroscopy, infrared (IR) spectroscopy, active thermography, X-ray diffraction and colour measurement [1]. In previous Raman spectroscopy research, it was discovered that the average peak intensity of aged specimens decreased in comparison with that of unaged specimens, while the average bandwidth of peaks in the Raman spectrum of aged specimens increased in comparison with that of unaged specimens [8]. However, a poor signal to noise ratio was produced at short wavelengths [9]. Nazare et al. [10] and Arrieta et al. [11] attempted to relate the tensile strength of outer shell fabrics to the absorption peaks of the IR spectrum within different regions. Nazare, et al. focused upon two ranges, 3550-2950 cm^{-1} and 1825-1625 cm^{-1}, while Arrieta, et al. examined a much broader region of the spectrum, 4000-500 cm^{-1}. Nazare, et al. found that the change in the characteristic peaks' intensity and broadening was consistent with the deterioration in tear and tensile strength of aged specimens after ultraviolet (UV) exposure, while Arrieta, et al. observed that the variation of the absorption peaks was more subtle following thermal aging even though the tensile strength of specimens decreased noticeably. Gralewicz and Wiecek [12] employed active thermography to detect defects in fire protective fabrics, but this method was unable to detect defects below a particular size which could be present during the initial stages of textile degradation. A connection between changes in crystallinity and mechanical strength was seen by Jain and Vijayan via X-ray diffraction [13]. Although this method shows potential, there are high cost associated with X-ray diffraction that may discourage its implementation. Visual methods may seem to be the most straightforward, but there are unique challenges associated with these methods, some of which are quite subjective. Slater has shown that textile performance may begin to degrade prior to any visual indication of deterioration, suggesting that a non-visual method is necessary to accurately determine the state of a garment [14]. In a previous study, the colour change experienced by a specimen was correlated with its tensile strength after experiencing thermal ageing [15]. Colour change was defined as the distance between the colours of the new and aged specimens measured and plotted in red-green-blue space. It was found that the correlation was heavily dependent upon the original colour of the specimen; dark fabrics would initially become lighter as the dye disappeared, but then would become darker once they began to char. In contrast, light coloured fabrics grew progressively darker with increasing thermal exposure. These phenomena are illustrated in Figures 1 and 2 with royal blue and yellow Nomex® IIIA fabrics respectively.

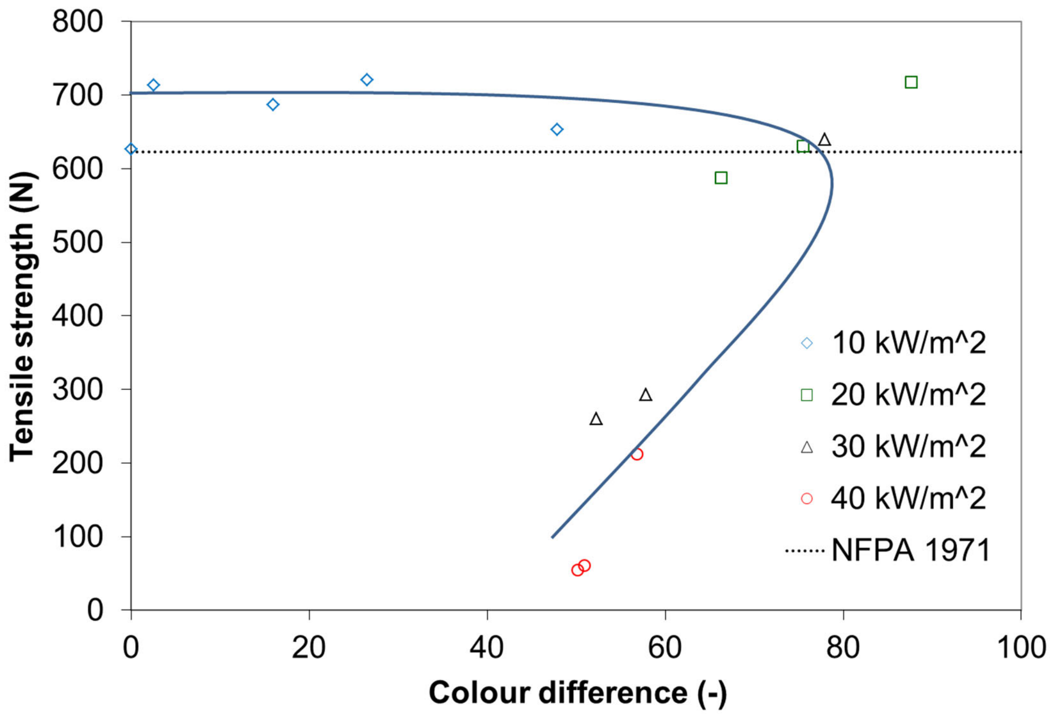

Fig. 1 The Relationship Between Tensile Strength and Color Difference Following Thermal Ageing of Royal Blue Nomex® IIIA Fabrics Using Different Heat Fluxes [1]

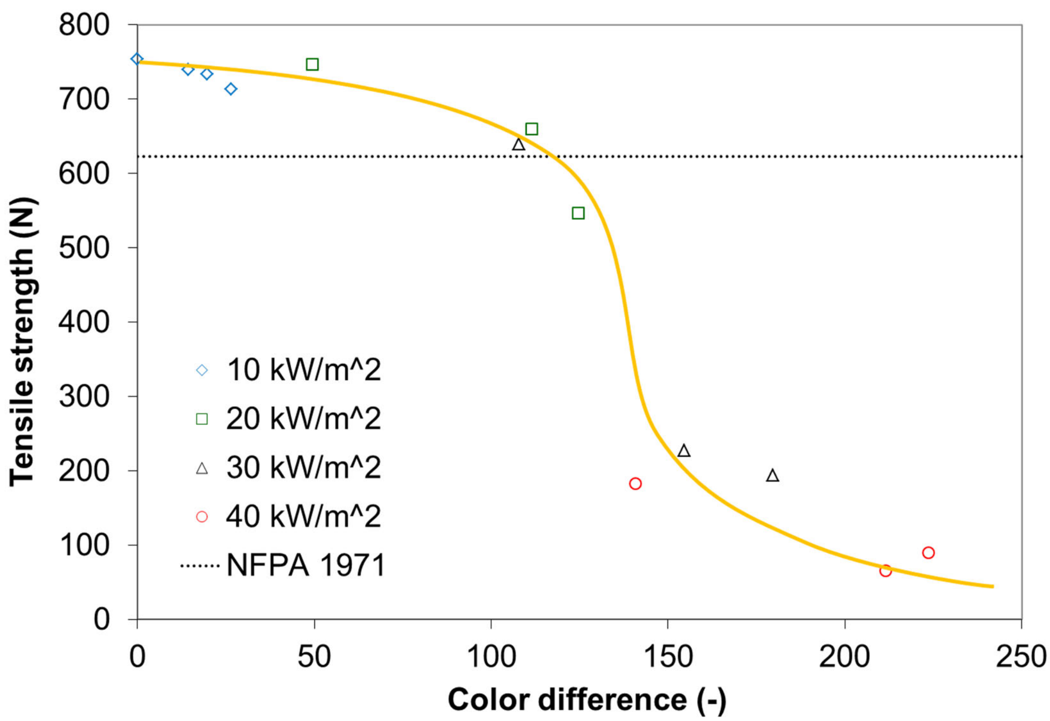

Fig. 2 The Relationship Between Tensile Strength and Color Difference Following Thermal Ageing of Yellow Nomex® IIIA Fabrics Using Different Heat Fluxes [1]

Near-infrared (NIR) spectroscopy uses the near-infrared portion (wavelength range of 780 to 2500 nm) of the electromagnetic spectrum. Similar to other techniques of spectroscopy, it is used for identification of compounds and investigation of material composition, but analysis is faster because of higher imaging speed and minimal specimen preparation [16]. A beam of infrared light with known wavelength is shone on the specimen. If the beam frequency is equal to the frequency of any type of vibrational motions of molecules in chemical bonds of the specimen, the beam can be absorbed at varying intensities. The radiation that is not absorbed is either transmitted through, or reflected off, the specimen. Using NIR spectroscopy, the chemical changes a textile undergoes can be monitored as it degrades.

Compared to IR spectroscopy, there has been limited research into applying NIR spectroscopy to the evaluation of in-use protective garments. In other areas, this technique has been applied to predict the density, stiffness and tensile strength of wood specimens ([17], [18], [19]). Hedrick et al. in particular noted that an accurate prediction employing wavelengths in the spectral range of 950-1850 nm could be developed using small, inexpensive instruments [19].

This paper will examine if NIR spectroscopy can be used to predict the tensile strength of fabrics used in firefighters' protective clothing and other thermal protective apparel that have been thermally aged using high heat fluxes. Multivariate linear regression has shown promise in the past for predicting the strength of other materials using NIR spectral data [20], so it will be applied here to the evaluation of protective clothing. It was hypothesized that chemical changes induced by thermal exposure which manifest as tensile strength changes could be correlated to changes evident in the corresponding NIR spectrum.

Methods

The fabric specimens used were Nomex® IIIA made of Type 462 Nomex® fibres (poly meta-aramid) with a surface weight of 203 g/m^2. Type 462 Nomex® is a blend of approximately 93% poly meta-aramid, 5% poly para-aramid, and 2% static dissipative fibre and is used in various types of thermal protective apparel such as wildland firefighting [21]. In the current work, four different colours of Nomex® IIIA were used: royal blue, red, yellow and dark blue.

Specimens were cut to 15 cm by 10 cm (6 in. by 4 in.) from the aforementioned fabrics, and were conditioned for at least 24 hours at 22 ± 2°C and 65 ± 2% relative humidity in a conditioning chamber. For thermal ageing the specimens were placed on a stand 25 mm below the conical heater of a cone calorimeter (Fire Testing Technology, East Grinstead, U.K.). The heat flux was set based on measurements made at a distance of 25 mm from the center of the heater by a Schmidt-Boelter heat flux gauge (Medtherm, Huntsville, AL) cooled by a water flow. A metal aperture constrained the exposed area (8.5 cm by 5.8 cm) to the central part of the specimen.

In order to determine the temperature history of the specimens during thermal ageing an infrared thermometer (Cyclops 300AF, Minolta/Land, Dronfield, UK) was employed to measure the temperature of the center point of the back side of the specimen when it was exposed in the cone calorimeter. A new specimen holder that was specially designed for cone calorimeter fabric testing in the vertical orientation was used in these tests [22]. This holder was developed because it is easier to make infrared temperature measurements in the vertical orientation. During the development process it was also shown that in the range of heat fluxes used in this study fabric temperatures measured in the cone calorimeter in the vertical and horizontal orientations should be very similar to each other. The infrared thermometer was connected to an Agilent 34970A data acquisition system (HP Agilent 34970A, Santa Clara, CA) which recorded the temperature approximately every 0.1 seconds.

In terms of intensity of thermal exposure, firefighting environments are often categorized into three regions which help describe the duration which firefighters are expected to be able to work safely within an environment: routine, ordinary, and emergency [23]. Each of these categories is defined by a range of heat fluxes and air temperatures:

- Routine – heat fluxes from 1 to 2.1 kW/m^2, temperatures from 10 to 60°C;
- Ordinary – heat fluxes from 2.1 to 25 kW/m^2, temperatures from 60 to 300°C; and
- Emergency – heat fluxes from 12.5 to 125 kW/m^2, temperatures from 300 to 1000°C.

Exposures to low heat fluxes in routine conditions may require a long time to cause noticeable deterioration in the specimens. As a result, heat fluxes of 10, 20, 30 and 40 kW/m^2 were selected for this part of the study, which represent ordinary conditions and the lower range of emergency conditions. Specimens were exposed at 10 kW/m^2 for 600, 1200 and 2400 s; at 20 kW/m^2 for 30, 150 and 300 s; at 30 kW/m^2 for 15, 30 and 60 s; and at 40 kW/m^2 for 10, 20 and 30 s. One specimen was tested for each heat flux/exposure time combination, for a total of 13 specimens per colour. Two extra exposure were used for royal blue specimens: 10 kW/m^2 for 15 s and 20 kW/m^2 for 60 s, such that 15 tests were made for the royal blue fabrics. The temperature histories of the specimens were also compared with thermogravimetric analysis (TGA) curves in order to explain the changes in the properties of the fabrics after thermal exposure. TGA experiments were run for the same fabrics at a heating rate of 20°C/min in an air environment using a TA Instruments Q500 Thermogravimetric Analyzer (New Castle, DE). The final temperature was set at 800°C for all TGA experiments. The mass of individual specimens was in the range of 8-12 mg and the samples were placed in high-temperature 100 µL platinum crucibles.

The tensile strengths of the new and thermally aged outer shell specimens were measured using a method similar to NFPA 1971 [3] and ASTM D5034-09 [24]. The tensile testing machine was an Instron 1122 (Norwood, MA), operated at a constant rate of extension of

200 mm/min. Jaw faces were covered with an anti-slip coating. The jaw dimensions were 25 mm (1 in.) perpendicular to the direction of applied force by 37.5 mm (1.5 in.) parallel to the direction of the applied force.

An NIR scan of each new and thermally aged sample was taken using a Cary 5G UV-Vis-NIR spectrophotometer equipped with a diffuse reflectance accessory (Agilent Inc., Mississauga, ON). A calibrated 50% reflectance Spectralor (Labsphere Inc., North Sutton, NH) standard was used to calibrate the full scale output. Spectrophotometer scanning parameters were set as indicated in Table 1. Results reported in this paper are the average of measurements made at three locations on the fabric.

Table 1 Spectrophotometer Scanning Parameters

Scanning Parameter	**Value**
Start Wavelength	2500 nm
Stop Wavelength	250 nm
Scan Rate	600 nm/min
Resolution	1 nm
Averaging Time	0.1 s
Spectral Band Width (SBW)	2 nm
Energy	1.00
Slit Height	reduced
Beam Mode	double
Source Changeover	350 nm
Detector Changeover	800 nm
Baseline Type	zero/baseline correction

Multivariate linear regression analysis was utilized to correlate tensile strength with the changes in the reflectance spectrum. Models of this type exhibit a form resembling that of equation 1,

$$Y = \alpha_0 + \alpha_1 \cdot X_1 + \alpha_2 \cdot X_2 + \ \dots + \alpha_n \cdot X_n + \varepsilon \qquad (1)$$

where Y is a dependent variable (tensile strength), X denotes an independent variable (reflectance percentage at a specific wavelength), α signifies the coefficient of the independent variables, n indicates the number of the independent variables, and ε represents the deviation of the predicted tensile strength value from the real value. A MATLAB® computer program was written to assess and order the subsets of regression equations according to statistical criteria such as R^2 and R_a^2 (adjusted R^2), and the number of independent variables in the regression equation. Finally, a few of the best regression equations were selected and their ability to predict the tensile strength of some testing points (specimens which were not incorporated in the development of the regression models, but were used to examine the model's accuracy) were examined.

Results & Discussion

Figure 3 shows the TGA curve for a red Nomex® IIIA fabric specimen. The mass loss curves of the other coloured fabrics are not shown, but the results were very similar, reflecting how all samples are made out of the same blend and possibly indicating that the chemical compositions of the different dyes are also similar. This also suggests that all fabrics, regardless of their colour, underwent comparable decomposition processes. At the early stages of the test, around 60°C, mass loss is observed to begin as a result of moisture removal. Dye removal commences at around 270-300ºC. Thermal degradation of this fabric starts to occur at about 400ºC, indicated by the considerable change in mass loss rate. Some performance aspects of the material are expected to change remarkably around the degradation temperature. By the time it reached 600°C, the specimen had lost almost 75% of its initial mass. Further information on the degradation of these materials, including scanning electron microscope images of the thermally aged fabrics, can be found in [1].

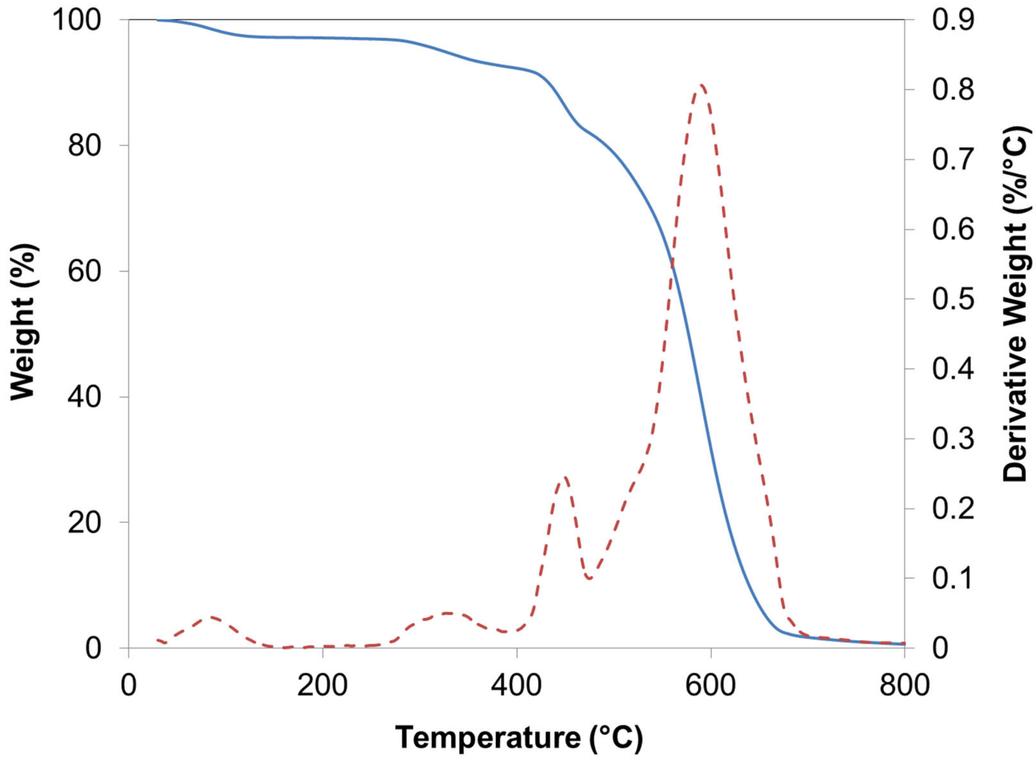

Fig. 3 TGA Curve for a Red Nomex® IIIA Specimen in an Air Environment

The time required for a specimen to reach a steady-state temperature varied depending upon the heat flux it was exposed to. Figure 4 shows the temperatures measured on the unexposed side of a royal blue Nomex® IIIA fabric during the first 30 s of heating. For heat fluxes of 30 kW/m^2 and 40 kW/m^2 temperatures reached approximately steady-state values after about 20 s. By 30 s, temperatures were considered to have reached steady-state for all heat fluxes. These trends were observed in tests of specimens of other colours. Temperature measurements and TGA results were used to help interpret visual observations and changes in tensile strength, which will be discussed later in the paper. It should also be noted that the conditions under which TGA data is taken are different from the conditions in the cone calorimeter, and therefore that care should be taken when interpreting these two sets of data. Previous research has also demonstrated that while an infrared thermometer measures a weighted average temperature of the fabric volume within its viewing area, this measurement can be different from temperatures at individual locations on the fabric surface [25].

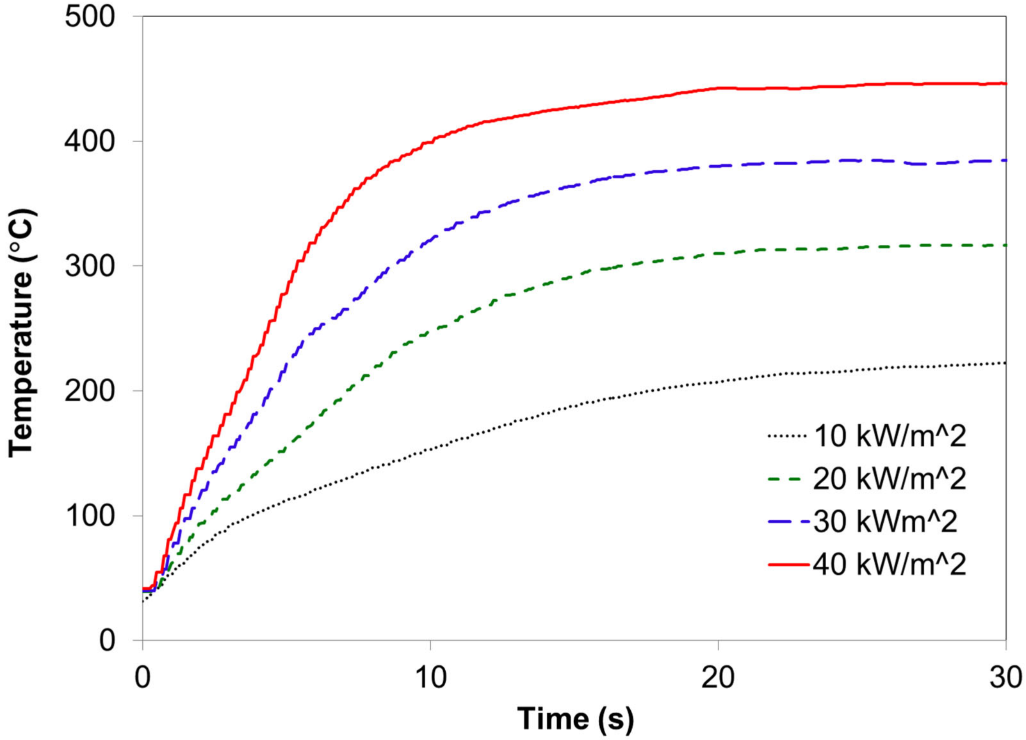

Fig. 4 Temperature Profile of Royal Blue Nomex® IIIA Specimens During the First 30 Seconds of Heating Using Various Heat Fluxes

Figure 5 displays the average tensile strength of the specimens after various levels of thermal exposure. The minimum tensile strength requirement in NFPA 1971 [3] is also shown. Specimens were not differentiated by colour in this particular analysis. One specimen of each colour for a total of four specimens were used to determine an average tensile strength for every condition. This was done because even if specimens are different in colour, they are composed of the same fibres and should perform similarly in a tensile test. Error bars on the columns indicate the standard error of the mean. The bias error reported by the manufacturers of the test equipment used in this research was negligible in comparison with the random error. As anticipated, lengthening the duration of an exposure for a given heat flux reduced the tensile strength of specimens. This was consistent with the findings of other researchers [26,27]. The decrease in tensile strength depended on the intensity of the thermal exposure. The tensile strength of specimens exposed to 10 kW/m^2, regardless of duration, resembled that of an unexposed specimen; this was consistent with the TGA and temperature measurements which indicated that little degradation was to be expected. Increasing the exposure duration from 600 s to 2400 s reduced the tensile strength by 5%. The tensile strength decreased more significantly when fabrics were exposed to 20 kW/m^2; tensile strength was reduced by around 20% by increasing the exposure duration from 30 s to 300 s. At higher intensities, the decrease in tensile strength in the early stages of thermal exposures was much more pronounced than in later stages. For 30 kW/m^2 exposures, the tensile strength was reduced by 55% when the duration of exposure increased from 15 s to 30 s. Continuing an exposure to this heat flux for an additional 30 s reduced tensile strength by only an additional 10%. 10 s of exposure to a heat flux of 40 kW/m^2 decreased the tensile strength of the specimen by 66%. An exposure of 20 s decreased the tensile strength by an additional 23%. However, increasing the length of exposure to 30 s did not decrease the tensile strength of the specimen further; in fact, a slight increase was observed. As this increase was smaller than the error bar, it was considered insignificant.

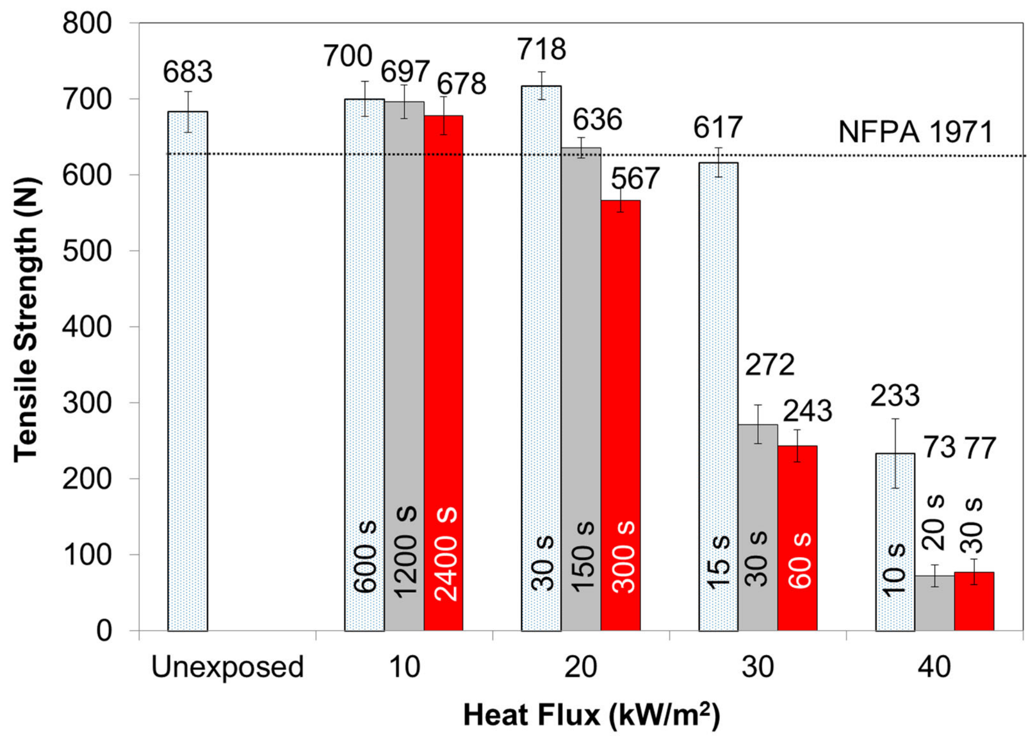

Fig. 5 Average Tensile Strength of All Specimens after Various Levels of Thermal Exposure (N=4)

Figure 6 shows the NIR spectra of unexposed fabric specimens of all colours. In the visible range of the spectrum (380 nm to 750 nm), large variations exist in the reflectance of each fabric at a particular wavelength; this was to be expected based on the differences in specimen colour. A literature review on wavelength bands in the NIR region concluded that wavelengths smaller than 1486 nm are sensitive to colour change, even though this extends beyond the visible spectrum [28]. For the remainder of the paper, only the region between 1500 and 2500 nm will be considered because it is not susceptible to colour variations. Within this range, reflectance values at a particular wavelength differed at most by 4% reflectance for each of the different colours of fabric.

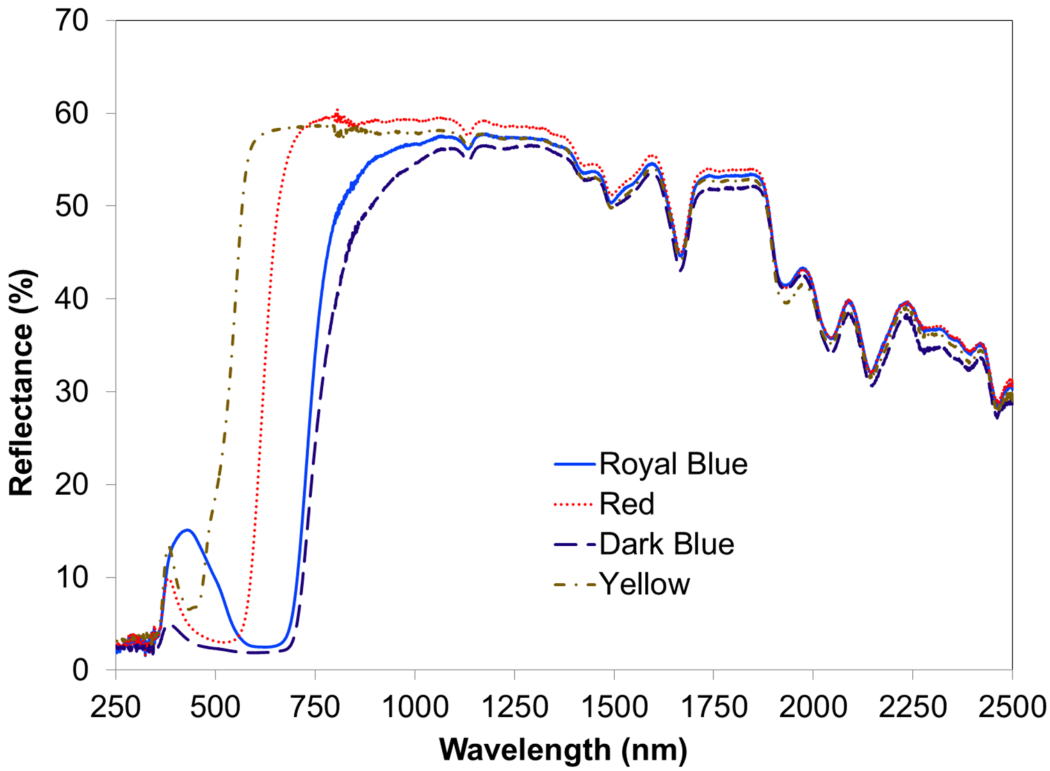

Fig. 6 Reflectance Spectra of Unexposed Specimens of Different Colours

The reflectance measurements reported in this paper are average values of measurements conducted at three different locations within the exposed area of the fabric. There was a good level of repeatability in the measurements. For reflectance spectra measured for unexposed specimens of each of the four colours of fabric between 1500 and 2500 nm, the standard deviation was within 5% of the mean for almost all reflectance measurements. This level of repeatability was also seen in the reflectance measurements after thermal ageing. For example, for each of two royal blue fabric specimens exposed to 20 kW/m^2 for 150 s the standard deviation was within 3% of the mean for almost all reflectance measurements between 1500 and 2500 nm on an individual fabric. Almost all of the mean values at an individual wavelength were within 5% of each other for the two fabric specimens. This level of repeatability is an indication of the repeatability of the measurement technique, as well as the uniform heating of the exposed portion of the fabrics; heat fluxes from the cone calorimeter were within 90% of the nominal value at all points within the exposed area of the fabric specimens [1].

Figure 7 includes photographs of Nomex® IIIA specimens after various thermal exposures. A small amount of dye began to come out after the 10 kW/m^2 exposure, but it is much more apparent following the 20 kW/m^2 exposure. By 30 kW/m^2 charring begins, and severe charring occurred on the specimens exposed to 40 kW/m^2. Figure 8 compares the reflectance spectra between 1500 and 2500 nm of the different coloured specimens exposed to 30 kW/m^2 for 30 s. After this level of thermal ageing, the specimens appeared to have sustained a significant amount of damage. The specimens of different colour appeared to have aged similarly as the NIR spectra did not differ from each other significantly. The largest difference appeared at the absorption band around 1950 nm where the behaviour of the dark blue sample diverged from that of the other specimens; examining the scale however, this difference is only about 3% reflectance in magnitude. Besides this, the spectra indicated that the fabrics underwent similar decomposition processes as was expected from the TGA results.

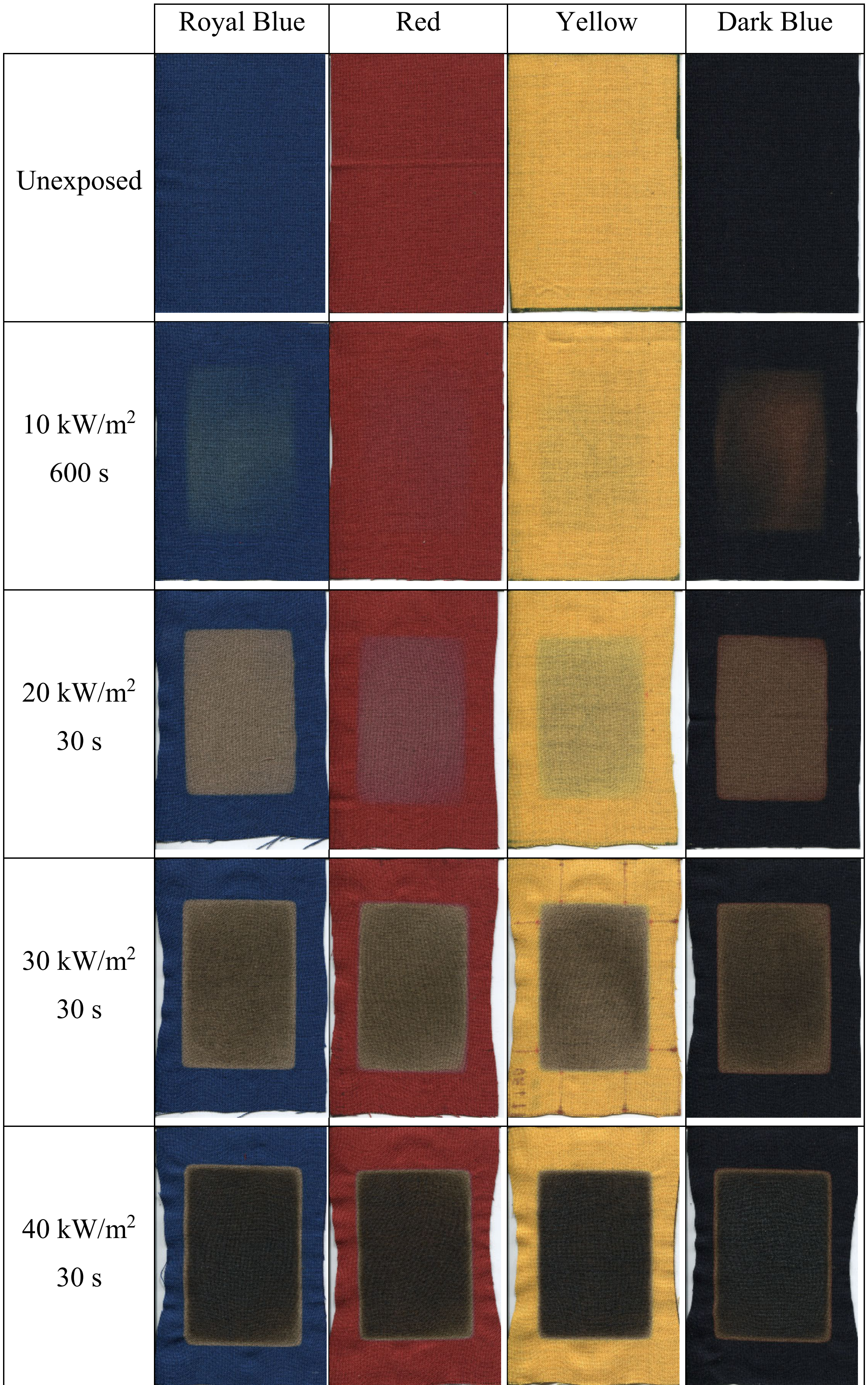

Fig. 7 Images of Nomex® IIIA Specimens After Various Thermal Exposures

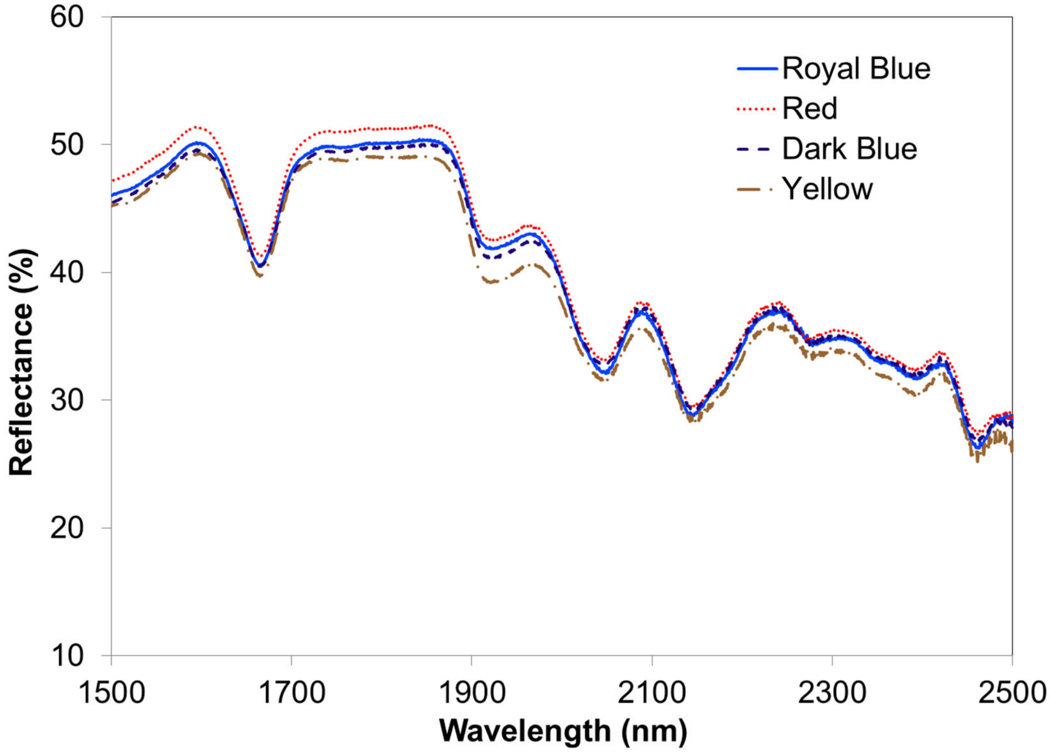

Fig. 8 Reflectance Spectra of Specimens Exposed to 30 kW/m^2 for 30 s

Figures 9-12 show the diffuse reflectance spectra of thermally aged royal blue specimens in comparison with that of the unexposed (new) specimen. Only spectra for royal blue specimens are displayed here because the spectral trend was similar for all fabric colours. In Figure 9, the reflectance spectra are very similar for all durations of exposure to 10 kW/m^2. As noted earlier, during exposures to 10 kW/m^2, the specimen temperature remained well below the key temperatures in the TGA curve (Figures 3 and 4). Hence, only slight changes might be expected in the molecular structure and corresponding physical properties (tensile strength) of the fabric even after prolonged thermal exposure. According to the TGA, dye removal starts around 300ºC which is similar to the maximum temperatures of the specimens during exposures to 20 kW/m^2. Therefore, dye removal could have influenced the reflectance spectra. As a result of more severe thermal exposures to 30 and 40 kW/m^2, the reflectance spectra in Figures 11 and 12 change similarly. The peaks and valleys in the spectra begin to change significantly, just as there was a decrease in tensile strength of up to 90% as compared to a new specimen. The observations in Figures 6 and 9-12 suggest that the tensile strength of thermally aged specimens may be correlated with the changes in the reflectance spectrum. This correlation seems to be stronger in the wavelength range of 1500-2000 nm, as the reflectance spectrum is more sensitive to thermal exposure in this range.

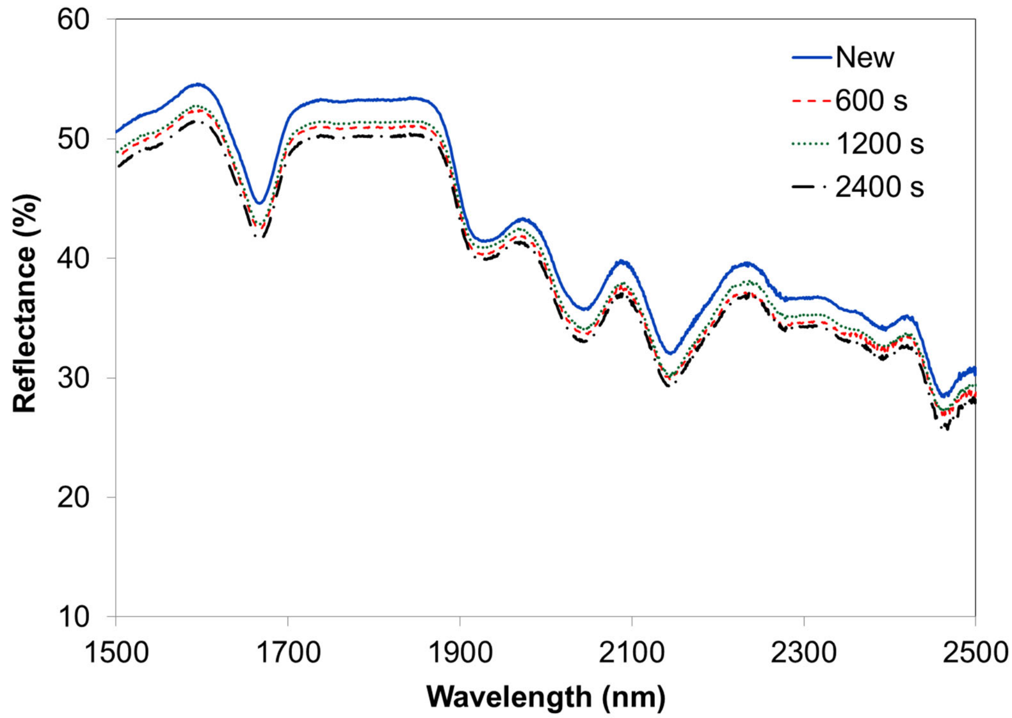

Fig. 9 Reflectance Spectra of Royal Blue Specimens Exposed to 10 kW/m² for 600, 1200 and 2400 s

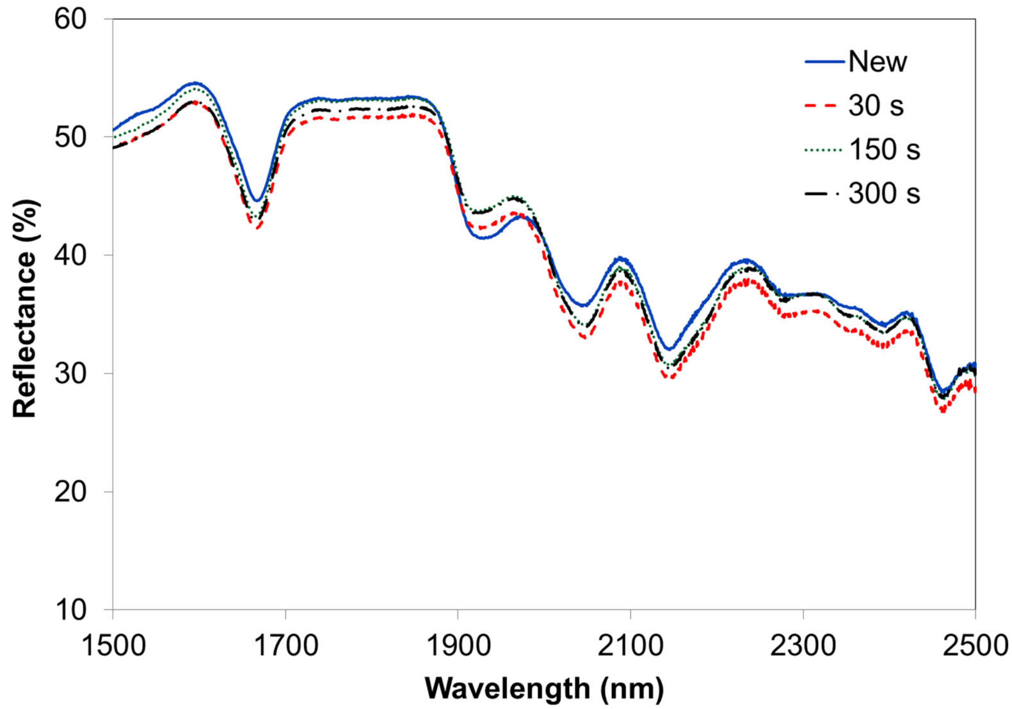

Fig. 10 Reflectance Spectra of Royal Blue Specimens Exposed to 20 kW/m^2 for 30, 150 and 300 s

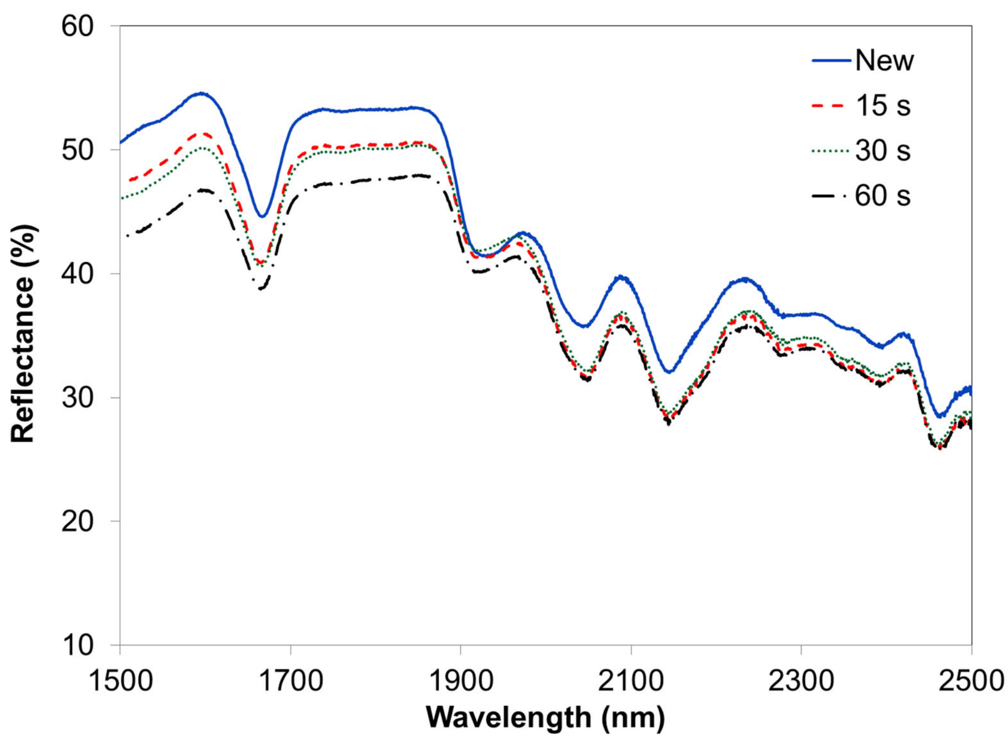

Fig. 11 Reflectance Spectra of Royal Blue Specimens Exposed to 30 kW/m^2 for 15, 30 and 60 s

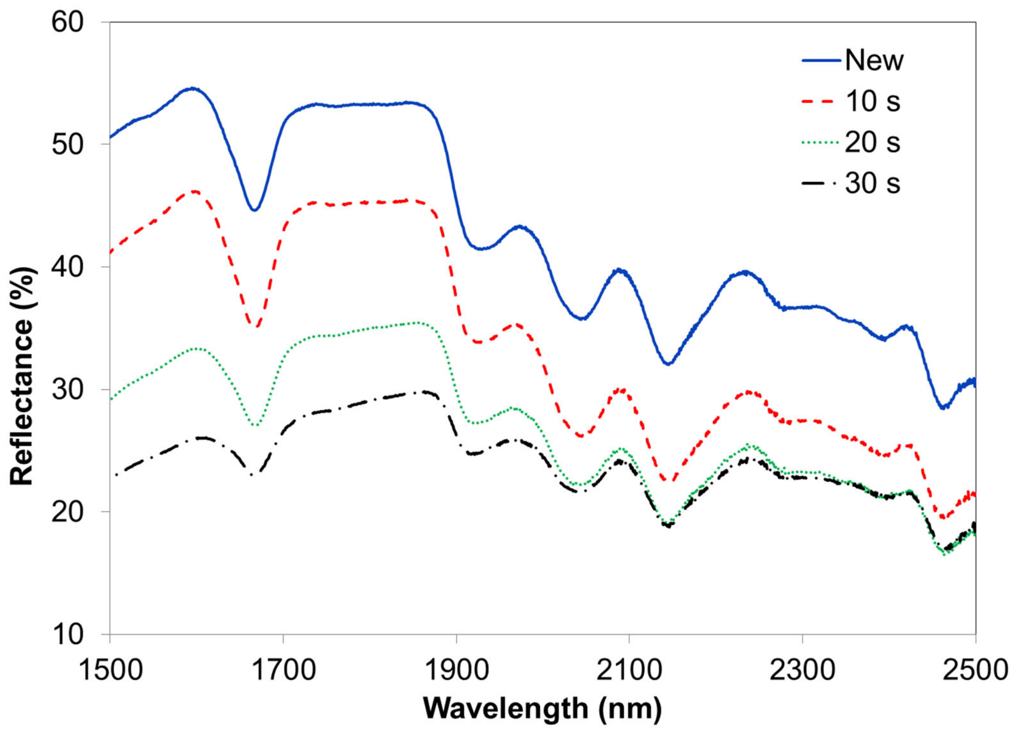

Fig. 12 Reflectance Spectra of Royal Blue Specimens Exposed to 40 kW/m^2 for 10, 20 and 30 s

Using the spectra of Figures 9-12, a multivariate linear regression model was developed to predict the tensile strength of thermally aged samples of the same material, by relating the spectral trend to the decreases in mechanical strength. The first step in developing the linear regression model was to choose an appropriate number of variables to employ. Spectral data are often highly correlated, meaning that not all wavelengths are necessary to ascertain the condition of a garment. Therefore, to simplify the implementation of a model, it is expected that a relatively small number of selected wavelengths can be used. To determine the number of wavelengths to use in the equation, a MATLAB® program was developed, which determined statistical criterion of interest for all possible subsets of the regression equation within the wavelength range 1500 – 2500 nm, using wavelengths at 100 nm intervals. An interval of 100 nm was selected for this preliminary, proof of concept analysis; more sophisticated wavelength selection will be performed in the future. Of particular interest was the R_a^2 (adjusted R^2) parameter, because it takes into account the number of independent variables used to make the equation. Mathematically, R^2 and R_a^2 are expressed as follows:

$$R^2 = \frac{\sum_{i=1}^{m}\left(\widehat{Y}_i - \bar{Y}\right)^2}{\sum_{i=1}^{m}(Y_i - \bar{Y})^2} \tag{2}$$

and

$$R_a^2 = 1 - (1 - R^2)\left(\frac{n-1}{n-p}\right) \tag{3}$$

where m is the number of observations of the dependent variable Y (tensile strength), $\hat{Y}$ is the predicted value of the dependent variable, $\bar{Y}$ is the mean of the actual values of the dependent variable in m observations, and p is the total number of coefficients in the regression equation. In order to avoid singular matrices in the derivation of regression equations and calculation of R_a^2, the maximum number of independent variables was set to two less than the number of observations. Hence, a regression equation could contain a maximum of 11 wavelengths for the red, yellow and dark blue samples because only 13 observations were taken for these fabrics. Fifteen observations were obtained for the royal blue so the maximum number of independent variables was 13 for this fabric. Although a resolution of 1 nm was obtained in the collection of reflectance data, wavelengths at 100 nm increments were used to select the number of independent variables to utilize. For instance, 2500, 2400, 2300, 2200, 2100, 2000, 1900, 1800, 1700, 1600, and 1500 nm were the only wavelengths that could be used in an 11 variable model.

Figure 13 shows the impact of the number of independent variables on R_a^2 for the royal blue fabric. Using a larger number of independent variables did not necessarily improve the predictive power of a model. This was because wavelengths that were not affected as significantly by chemical changes in the fabrics began to be included. Using the MATLAB® code, the three wavelengths that produced the highest value of R_a^2 for each specimen colour were determined. These wavelengths are shown in Table 2. Despite only using three variables, the values of R_a^2 are at least 0.95 for three of the fabrics, and 0.85 for the other fabric. It is of interest that all four models contain the wavelength 1600 nm, which suggests that it is strongly connected to changes in the structural integrity of the fabric caused by thermal ageing.

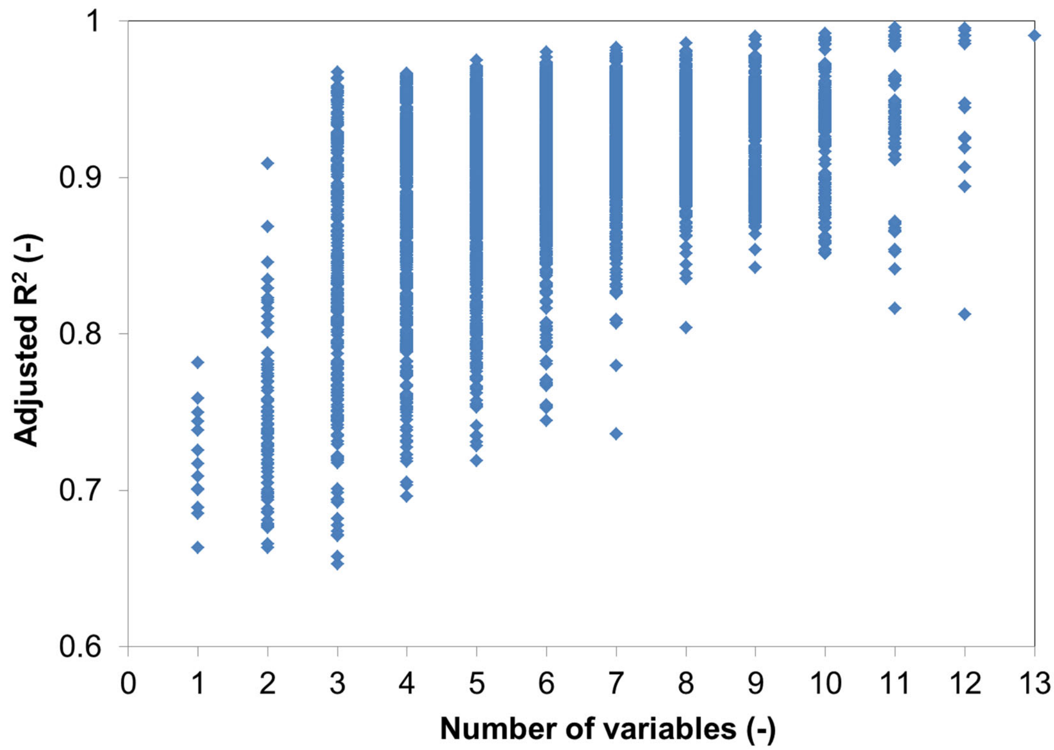

Fig. 13 Range of Adjusted R^2 (R_a^2) Values in Equations Made of a Particular Number of Variables for Royal Blue Nomex® IIIA Specimens

Table 2 Wavelengths of the Most Accurate Three-variable Regression Equations and Comparison Between Predicted and Measured Tensile Strengths

Colour	**R_a^2**	**Wavelengths (nm)**			**Percentage Error Between Predicted and Measured Tensile Strength**		
		1	2	3	5 kW/m^2 3600 s	15 kW/m^2 1200 s	25 kW/m^2 180 s
Royal Blue	0.97	1500	1600	2000	-20.9%	-31.6%	34.0%
Red	0.99	1600	1800	2300	-23.5%	-34.1%	-5.8%
Dark Blue	0.95	1600	1800	2500	-16.9%	-22.4%	18.7%
Yellow	0.85	1500	1600	1900	-22.2%	-22.3%	44.8%

Even though these R_a^2 values imply that these linear equations may fit training data points well within the test matrix, they do not give any information about how accurately the linear equations predict the tensile strength of fabrics that were not included in the training data (testing points). In order to investigate this issue, three additional exposures were used to thermally age one specimen of each colour: 5 kW/m^2 for 3600 s, 15 kW/m^2 for 1200 s and 25 kW/m^2 for 180 s. Reflectance measurements for these thermally aged fabrics were made and input into the linear regression model to evaluate how accurately it predicted the measured tensile strength values. Table 2 and Figure 14 illustrates the error in testing point predictions for the royal blue Nomex® IIIA samples. Errors in predicted strengths are pointed out by labels beside each point. Among the three testing points, the model predicted lower tensile strengths than measured values for moderate exposures (5 kW/m^2 and 15 kW/m^2 which represent ordinary conditions), and overestimated the strength of the fabric which experienced the more severe condition (25 kW/m^2 which represents an emergency condition). This pattern was also exhibited for the other colours of fabrics with red being the exception; the three-variable regression model underestimated the strength of all three testing points for the red fabric. Testing point errors for red, yellow and dark blue fabrics were similar in magnitude to the royal blue values, the largest error being the overestimation of the strength of the yellow fabric for the 25 kW/m^2 exposure (45%).

It should be noted that a model should provide a conservative prediction of tensile strength. If a garment's strength is overestimated, then it is possible that it could remain in service while not providing the minimum desired strength. Hence, a model that underestimates tensile strength would be more beneficial in the practical evaluation of protective clothing than a model that overestimates tensile strength. Alternatively, a safety factor could be incorporated into the model to ensure tensile strength estimates are conservative.

In order to consider the effect of wavelength regions on the accuracy of predictive equations, the NIR spectrum was divided into two portions and regression equations were created for each region. Analysis was limited to royal blue fabrics. The first region spanned from 1500 nm to 1900 nm in intervals of 25 nm, while the second region extended from 1900 nm to 2500 nm in intervals of 50 nm. The specific wavelengths applied in each regression equation are shown in Table 3. A higher R_a^2 was produced using the 1500 – 1900 nm region, which was very similar to the R_a^2 in Table 2 for the model based on the entire spectrum. This observation was in agreement with the observation that reflectance spectra were more sensitive to thermal exposure in the region 1500 – 1900 nm as was seen in Figures 9-12.

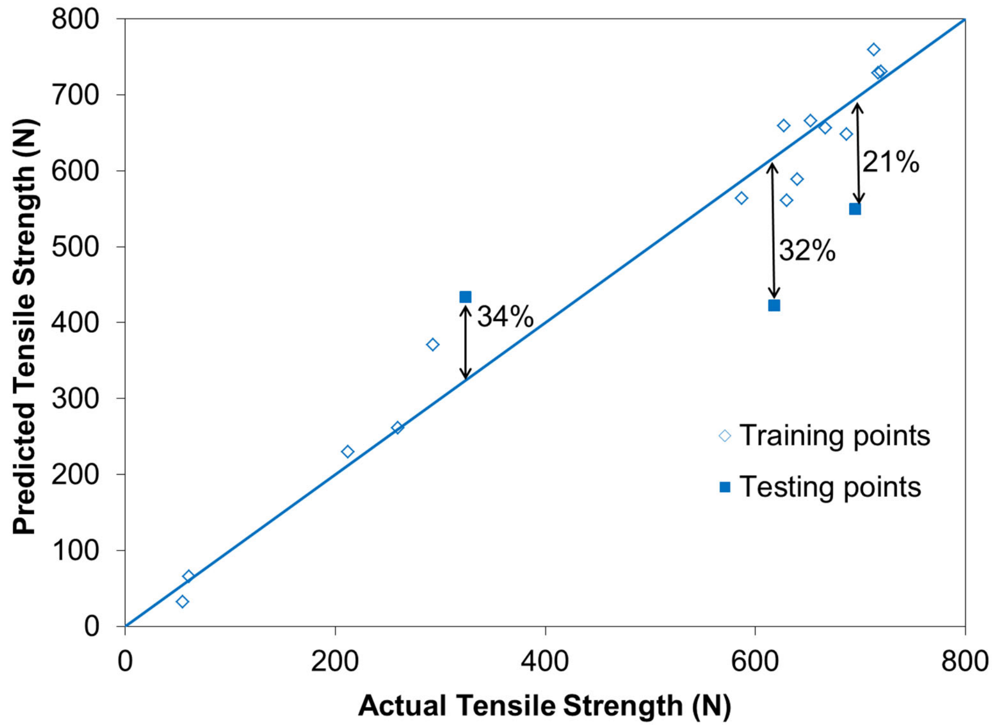

Fig. 14 Ability of the Royal Blue Nomex® IIIA Three-Variable Linear Regression Model to Predict the Tensile Strength of Testing Points

Table 3 Wavelengths of the Most Accurate Three-Variable Regression Equations for Royal Blue Nomex® IIIA Fabrics Using Specific NIR Regions and Comparison Between Predicted and Measured Tensile Strength Values

Wavelength Region (nm)	**R_a^2**	**Wavelengths (nm)**			**Percentage Error Between Predicted and Measured Tensile Strength**		
		1	2	3	5 kW/m^2 3600 s	15 kW/m^2 1200 s	25 kW/m^2 180 s
1500 – 1900	0.97	1500	1600	1700	-16.6%	-19.3%	54.7%
1900 - 2500	0.88	2200	2450	2500	12.3%	3.6%	48.5%

Table 3 also compares how well the models based on the two wavelength ranges predict the tensile strength for the three testing points. Even though the model based on the 1500 – 1900 nm wavelength region had a higher R_a^2, it did not predict the three testing points as accurately as the model based on the 1900 – 2500 nm region. It was able to predict the tensile strength of the two specimens exposed to ordinary conditions conservatively. In contrast, the model utilizing the 1900 – 2500 nm region predicted the three testing points more accurately, but every prediction overestimated the tensile strength of the specimens. The royal blue three-variable model which applied wavelengths from the entire spectral range of 1500 – 2500 nm performed similarly to the 1500 – 1900 nm version in terms of predicting the testing points. This is to be expected because both models employ two wavelengths that are identical, 1500 nm and 1600 nm, and may indicate that reflectance values obtained at these wavelengths are critical to determining structural changes that occur in fabrics undergoing thermal ageing.

To try and develop a more accurate regression equation, another model was developed using wavelengths which correspond to maximum and minimum points in the reflectance spectrum of royal blue fabric specimens. The following were observed to be wavelengths at critical points: 1600, 1700, 1750, 1925, 1975, 2050, 2100, 2150, 2250, 2275, 2400, 2425, and 2475 nm. From these points, the best fit three-variable model was constructed using the MATLAB® code. Ideally, this equation would reflect wavelengths tightly linked to structural changes that occur within the fabrics. Table 4 displays the wavelengths that were selected and the R_a^2 value that was achieved.

Table 4 Wavelengths of the Three-variable Regression Equation Using Selected Wavelengths Based on Peaks and Valleys in the NIR Spectrum and Comparison Between Predicted and Measured Tensile Strength Values

R_a^2	Wavelengths (nm)			Percentage Error Between Predicted and Measured Tensile Strength		
	1	2	3	5 kW/m^2 3600 s	15 kW/m^2 1200 s	25 kW/m^2 180 s
0.84	1600	1700	1750	-3.9	-19.2%	29.6%

Though the R_a^2 is lower than that of the other models, the model was able to predict the tensile strength of the two specimens exposed to ordinary conditions more accurately than the other models, and both predictions were conservative for these conditions, as seen in Table 4 and Figure 15. The error for the emergency condition testing point was higher than the other two testing points, but was still lower than for the other models. However, the model did overpredict the tensile strength at this point.

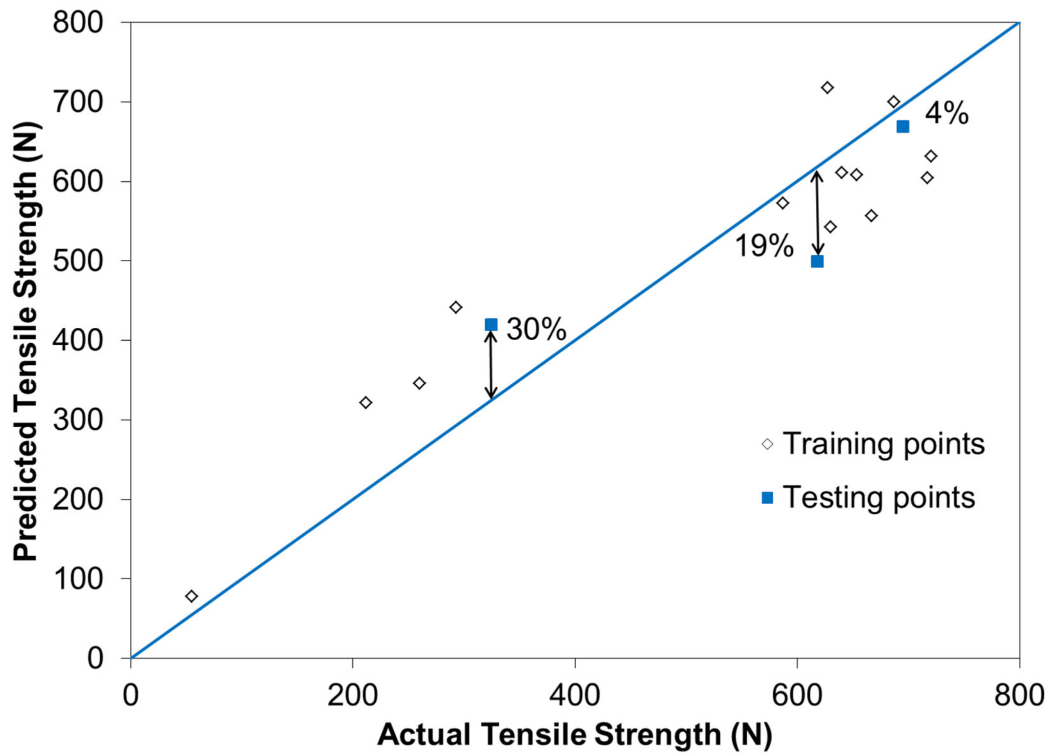

Fig. 15 Ability of Royal Blue Nomex® IIIA Three-Variable Linear Regression Model to Predict the Tensile Strength of Testing Points Using Selected Wavelengths Based on Peaks and Valleys in the NIR Spectrum

One issue in this preliminary study is that there was a lack of training data for tensile strengths between 300 N and 600 N. This was because the exposures were selected based on only four heat fluxes as part of a larger project [1]. These exposures resulted in aged fabrics with tensile strengths of more than 600 N and less than 300 N. An alternative approach would be to select exposures that would produce a range of degradation (e.g., selecting one heat flux and varying exposure time to produce a range of tensile strength values). If training data was available over a wider range of tensile strengths, it would be expected that a more accurate model could be developed. However, this proof-of-concept study did demonstrate the potential for using NIR reflectance measurements at a limited number of wavelengths to predict the tensile strength of thermally aged fabrics used in firefighters' protective clothing. This method could allow for the development of relatively low cost devices that could be used to assess in-use protective clothing, helping fire departments to better evaluate the expected performance of this clothing and to make more informed decisions about whether it should be retired, which would increase firefighter safety.

Conclusions & Future Work

This study evaluated the potential for using NIR reflectance measurements to predict tensile strength of single-layer Nomex® IIIA fabrics of different colours after they were exposed in the cone calorimeter to heat fluxes of 10 to 40 kW/m^2, which represent ordinary to emergency conditions faced by firefighters. NIR spectra were obtained using diffuse reflectance spectroscopy, and reflectance values between 1500 and 2500 nm were correlated with results of the tensile tests through multivariate linear regression. It was shown that fabric colour had a minimal effect on NIR spectra of the thermally aged fabrics, which would be advantageous for a non-destructive test method to evaluate in-use firefighters' protective clothing.

While regression models with up to 11 variables were investigated, it was found that even a three-variable regression model could predict tensile strength fairly accurately. Three different three-variable regression models, which were based on wavelengths between 1500 and 1900 nm, 1900 and 2500 nm, and wavelengths at which peaks and valleys occurred in the spectra were investigated further. The results of these studies indicated that there is the potential to develop models based on NIR measurements at a small number of wavelengths, which could be used to predict the remaining tensile strength of fabrics used in firefighters' protective clothing. As relatively inexpensive spectrophotometers could be designed to measure the reflectance at a few wavelengths this method could be implemented practically in the field.

There are a number of limitations of this proof-of-concept study, which would need to be addressed before this NIR method could be used in practice. Thermally aged fabrics in this study had tensile strengths of less than 300 N and more than 600 N; incorporating NIR training data at intermediate tensile strength values would be expected to improve the ability of linear regression models to predict tensile strength. While this study demonstrated the potential to use NIR reflectance for single-layer Nomex® IIIA fabrics used in wildland firefighting, the ability of this method to predict tensile strengths for a wider range of fabric types and weights will need to be demonstrated. While single exposures to high heat fluxes were considered in this study, the ability of the NIR method to predict changes in tensile strength due to other types of ageing, such as ultraviolet radiation and abrasion will need to be evaluated, along with combined exposures (e.g., multiple exposures to high heat fluxes and UV radiation), as would occur in the field. In the field, protective clothing will become soiled; therefore it will be important to determine whether the NIR technique can differentiate between changes in the fabric due to soiling, dye changes and thermal degradation. Finally, while this study only considered single-layer or outer shell fabrics, the ability of the NIR methods to assess other parts of a firefighters' protective ensemble, such as the moisture barrier and thermal liner should be evaluated.

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